

# PATENT SPECIFICATION

NO DRAWINGS

839,805



Date of Application and filing Complete

Specification: June 10, 1958.

No. 18489/58.

Application made in United States of America on June 10, 1957.

Complete Specification Published: June 29, 1960.

Index at acceptance :—Class 2(6), P7A, P7C(2:3:14B: 16A:20B:20C: 20D1:20D2: 20D3), P7D1(A: X), P7(K9:T2D), P9A, P9C(14A:16A:20B:20D1:20D3), P9(D1A1:K7:T2D).

International Classification :—C08f.

## COMPLETE SPECIFICATION

### Sprayable Compositions

We, MONSANTO CHEMICAL COMPANY, a Corporation organised under the Laws of the State of Delaware, United States of America, of Lindbergh and Olive Street Road, St. Louis 24, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to sprayable compositions containing film forming copolymers which are soluble in mild alkali and which are particularly useful for hair sprays.

The available hair sprays exhibit a variety of disadvantages in use. When sprayed onto the hair, many such products leave the hair coated with a tacky film which is shiny or lacquery in appearance. Other materials leave white flakes when the hair is combed. Still others are difficult to remove by washing.

The object of this invention is to provide materials which when used as hair sprays possess the proper film-forming and solubility properties to form a thin transparent non-shiny film which does not gel or become sticky in water and which is readily soluble in mild alkali and easily removed by washing.

According to the present invention there is provided a sprayable composition which comprises a solution, in an anhydrous alkanol containing one to four carbon atoms, of an alkyl ester of a copolymer of maleic anhydride and an olefin containing two to four carbon atoms, the copolymer having been esterified to the extent of 50-70% with an alkanol containing one to four carbon atoms and, as a propellant herefor, a halogenated alkane having one to three carbon atoms in the molecule.

The resinous materials utilised in the compositions of this invention are the half esters of copolymers of maleic anhydride with an olefin containing from 2 to 4 carbon atoms. Under the usual polymerisation conditions

for forming the copolymers the olefin and maleic anhydride combine in equimolar proportions. Methods are available which are at least partially effective in producing copolymers in which the mol ratio of olefin to maleic anhydride may be varied from 40 : 60 to 60 : 40. Copolymers which have been found to be effective in hair sprays are those having a molecular weight of from 25,000 to 70,000.

The esterification of the copolymers is a substantially spontaneous reaction if the half ester is desired. Solution of the copolymer in an excess of the desired alcohol is sufficient. Under these circumstances only the half ester is formed and any further esterification requires the presence of an acid catalyst and heating. Copolymers esterified up to 70% may be used provided the catalyst and the water formed in the esterification reaction are removed. Since the solvent required for the sprays of this invention is an anhydrous alkanol, the copolymer will be at least 50% esterified by dissolving it therein. The amount of esterified copolymer to be used may be 0.5 to 5 parts by weight per 100 parts of spray composition.

The copolymers used should be dissolved in an anhydrous alkanol having from one to four carbon atoms. The solvent may comprise 25-50% by weight of the total composition. If an unesterified copolymer is used as a raw material for preparing the spray composition, the amount of alkanol consumed in forming the half ester *in situ* should be taken into consideration.

If a plasticiser is desired, it may be used in an amount of up to 25 parts by weight per 100 parts of resin. Substantially odourless ester type plasticisers such as the dialkyl phthalates, for example, the dioctyl phthalates and diethyl phthalate; the alkyl phthalyl alkyl glycolates, such as butyl phthalyl butyl glycolate; the alkyl esters of polymethylene dicarboxylic acids such as adipates and sebacates and

[Price 3/6]

Price 25p

mixtures thereof may be used so long as they are soluble in the alkanols employed.

The aerosol propellant to be used in the compositions is a liquefied haloalkane which 5 exerts a total pressure of from 25-50 lbs./sq.in. at room temperature. The most satisfactory of these compounds are fluorine and chlorine substituted methane and ethane including trichlorofluoromethane, dichlorodifluoromethane, 10 methane, trifluorochloromethane and 1,2-dichloro-1,1,2,2,-tetrafluoroethane, or a mixture of any two or more thereof. Particularly suitable is a 50-50 mixture of trichlorofluoromethane and dichlorodifluoromethane. 15 The amount of propellant may range from 49 to 74% by weight of the total composition. The propellant is added to the solution of the ester after the latter has been placed within a pressure container equipped with suitable 20 valve release means.

Various conventional additives such as lanolin, non-drying oils, dyes, waxes and pigments may be added to the solution in small amounts to vary the properties of the 25 spray compositions and to make them suitable for application to different types of hair. Lanolin is particularly desirable to help restore the natural condition of the hair. In addition, a small amount of an alcohol- 30 soluble perfume may be added for aesthetic appeal.

The compositions of this invention may be sprayed onto dry or damp hair to provide a thin transparent film enhancing the natural 35 lustre of the hair without imparting a lacquered appearance to it. The deposited films have sufficient strength to keep the hair in place but insufficient to render it stiff. The composition dries quickly to a non-tacky state 40 which does not flake on combing but which is easily removed by washing with water containing a mild soap or commercial shampoo preparation.

The compositions of this invention are also 45 useful for other purposes for which sprayable film-forming materials which are soluble in mild alkali are needed. For example, they may be coloured and used as a sprayable shoe polish which will not be affected by water but 50 which can be removed by soap and water.

By proper colour formulation, it is possible to use the compositions to make frequent changes in shoe colours. Thus ladies' white shoes can be coloured to match one evening 55 gown, then washed and recoloured to match a different gown. For this application other volatile solvents such as acetone and methyl ethyl ketone may be used if desired.

The compositions may also be modified by 60 hard and soft waxes to provide floor and automobile finishes.

The following examples illustrate the nature of this invention and the manner in which it may be performed. Where parts are men- 65 tioned they are parts by weight.

#### EXAMPLE 1

Dissolve 1.5 parts of an ethyl half ester of a copolymer of ethylene and maleic anhydride having a molecular weight of substantially 25,000 in 30 parts of anhydrous ethanol. 70 Place the solution in a pressure container fitted with a spray nozzle and pressurise the solution with 70 parts of a 50-50 mixture of trichlorofluoromethane and dichlorodifluoromethane. When sprayed on newly waved 75 human hair, a thin transparent non-glossy film forms which holds the wave in place. The treated hair may be combed repeatedly without any evidence of flaking. On washing with warm water and soap or conventional 80 shampoo preparations, the film dissolves quickly and completely.

The following compositions were made up in the same way as that described in Example 1:—

#### EXAMPLE 2

Ethyl half ester of propylene- maleic anhydride copolymer- molecular weight substan- tially 30,000 .. .. .	3 parts	90
Trichlorofluoromethane ..	30 parts	
Dichlorodifluoromethane ..	30 parts	
Anhydrous propanol .. ..	40 parts	

#### EXAMPLE 3

Propyl half ester of ethylene- maleic-anhydride copolymer- molecular weight substan- tially 30,000 .. .. .	1.5 parts	95
1,2-dichloro-1,1,2,2,-tetra- fluoroethane .. .. .	4.0 parts	100
Trichlorofluoromethane ..	20 parts	
Anhydrous ethanol .. ..	40 parts	

#### EXAMPLE 4

Methylisobutyl half ester of ethylene-maleic-anhydride copolymer-molecular weight substantially 40,000 .. ..	1 part	105
Anhydrous ethanol .. ..	40 parts	
Dichlorodifluoromethane ..	20 parts	
1,2-dichloro-1,1,2,2,-tetra- fluoroethane .. .. .	40 parts	110

#### EXAMPLE 5

A typical formulation effective for a wide range of hair conditions is as follows:—

Ethyl half ester of ethylene- maleic-anhydride copolymer- molecular weight substan- tially 25,000 .. .. .	1.5 parts	115
Butyl phthalyl butyl glycolate ..	0.25 part	
Lanolin .. .. .	0.3 part	120
Anhydrous ethanol .. ..	30 parts	
Trichlorofluoromethane ..	35 parts	
Dichlorodifluoromethane ..	35 parts	

#### WHAT WE CLAIM IS:—

1. A sprayable composition which com- 125 prises a solution, in an anhydrous alkanol containing one to four carbon atoms of an alkyl ester of a copolymer of maleic anhydride and an olefin containing two to four carbon atoms, the copolymer having been esterified 130

to the extent of 50-70% with an alkanol containing one to four carbon atoms and, as a propellant therefor, a halogenated alkane having one to three carbon atoms in the molecule.

2. A composition according to Claim 1 in which the alkyl ester of the copolymer is an ethyl half ester of an ethylene-maleic anhydride or of a propylene-maleic anhydride copolymer.

3. A composition according to either of Claims 1 or 2 in which the alkyl ester is that of the alkanol in which it is dissolved.

4. A composition according to any of the preceding claims in which the alkyl ester is present in an amount of 0.5 to 5 parts by weight per 100 parts of composition.

5. A composition according to any of the preceding claims which includes, as an additional ingredient, a plasticiser for the ester copolymer which is substantially odourless and soluble in the alkanol used as solvent for the copolymer.

6. A composition according to any of the preceding claims which includes, as an additional ingredient, lanolin.

7. A composition according to any of the preceding claims in which the halogenated alkane is trichlorofluoromethane, dichlorodifluoromethane, trifluorochloromethane, 1,2-dichloro-1,1,2,2-tetrafluoroethane or a mixture of any two or more thereof.

8. A composition according to Claim 7 in which the halogenated alkane is a 50-50 mixture of trichlorofluoromethane and dichlorodifluoromethane.

9. A sprayable composition according to Claim 1 and substantially as hereinbefore described.

10. A method of producing a sprayable composition which comprises preparing a solution, in an anhydrous alkanol containing one to four carbon atoms, of an alkyl ester of a copolymer of maleic anhydride and an olefin containing two to four carbon atoms, the copolymer having been esterified to the extent of 50-70% with an alkanol containing one to four carbon atoms and introducing into said solution, in a pressure container, a sufficient quantity of a halogenated alkane having one to three carbon atoms in the molecule to act as a propellant therefor.

11. A method according to Claim 10 in which the alkyl ester is the ethyl half ester of an ethylene-maleic anhydride or of a propylene-maleic anhydride copolymer.

12. A method according to either of Claims 10 or 11 in which the alkyl ester is that of the alkanol in which it is dissolved.

13. A method according to any of Claims 10-12 in which the halogenated alkane is trichlorofluoromethane, dichlorodifluoromethane, trifluorochloromethane, 1,2-dichloro-1,1,2,2-tetrafluoroethane or a mixture of any two or more thereof.

14. A method of producing a sprayable composition according to Claim 10 and substantially as hereinbefore described.

STEVENS, LANGNER,  
PARRY & ROLLINSON,  
Chartered Patent Agents,  
Agents for the Applicants.